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BREAKING EMULSIONS IN NAVY BILGE COLLECTION AND TREATMENT SYSTEMS

Naval Research Laboratory,
Washington, D. C.

November 1976

Breaking Emulsions in Navy Bilge Collection and Treatment Systems

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The new bilge waste collection and treatment system, which serves as the collector, transporter and gravity separator for ship's bilge waste, has been shown to be a suitable medium for the application of chemical demulsification techniques. Chemical demulsification methods are especially suitable for emulsified oily wastes which are reluctant to separate into their constituent phases. Certain quatenary ammonium compounds have been shown to be highly effective demulsifiers over a wide range of concentration and temperature in a series of laboratory tests. The demulsifiers

(Continues)

20. Abstract (Continued)

were also found to be relatively insensitive to the type of oily waste and also performed well in the presence of particulate matter. A field demonstration of the demulsifiers supported the laboratory tests.

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BREAKING EMULSIONS IN NAVY BILGE COLLECTION
AND TREATMENT SYSTEMS

I. Introduction

Environmental Protection Agency requirements necessitate removal
of oil from oily wastes before discharge from Naval ships or installa-
tions into environmental waters. Specifically, the Federal Pollution
Control Acts of 1969, as amended in 1972 with DOD Directives 5100.50
and 6050.1 together with OPNAVINST 6240.2 call for implementation of
a new level of environmental pollution control practices. As a result
it has been necessary to drastically change the previous methods used
in the treatment and disposal of waste waters to meet the new regula-
tions. Refinements in the processing of oily wastes are expected to
improve within the framework of increasing restrictions on the allowable
levels of pollutants up to the FY-85 Standards which call for "Zero
Discharge of Pollutants". At this point final specific limits on
individual pollutants will be established by law.

Within the framework of increasing controls on the discharge of
oily waste pollutants into the environment the new bilge waste collec-
tion and treatment system represents an intermediate solution to this
difficult problem (1). The system consists of: (a) a waste oil raft
(donut) which serves as the collector, transporter and gravity separator
for ship's bilge waste and (b) a mobile modular oil/water separation and
removal (OWS&R) subsystem. Ideally, the OWS&R subsystem maintains the
donut by removing and storing gravity-separated oil and sludge, mechani-
cally separating oil/water emulsion via a filter/coalescer and circulating
fresh seawater through the donut to prevent stagnation. The capacity
of the donut is 26,000 gallons. The OWS&R subsystem contains a 100 GPM
pump which can be attached to the intake in the reskimming boxes and
a 350 GPM pump to remove the oxygen-depleted bilge water remaining in the
donut.

While the new waste oil raft with its OWS&R subsystem represents
a significant advance in the handling and treatment of oily bilge waste
waters, operational problems in the separation of oil and water can be
expected in the presence of surface-active material (1,2). However, a
vast literature exists on methods which are presumably useful in breaking
both water-in-oil and oil-in-water emulsions (3,4). The following
methods are generally used in practice:

Note: Manuscript submitted November 17, 1976.

(a) settling techniques

(b) centrifugation

(c) filtration, filter coalescer

(d) heating or distilling at various pressures

(e) electrical treatment

(f) chemical agents

The first four techniques may be classified as physical methods. They are, in general, somewhat inefficient except for the case of relatively unstable emulsions. In many cases an accumulation of unresolvable "sludge" occurs which interferes with operations and must be removed. However, interest in these devices continues as evidenced by their continued presence in the current patent literature. Electric treatment involves the development of a potential difference across the emulsion system whereby the stabilizing interfacial films are ruptured as a result of the deformation of the emulsified particles caused by the electric field. In some cases electrophoresis is combined with electrochemical effects (production of iron hydroxide which entangle the oil globules that subsequently condense in rusty-colored flakes). While electric treatment is superior to the mechanical methods previously mentioned, special equipment is required and the method becomes less efficient when the stabilizing interfacial film in the emulsion is particularly resilient and tough. Chemical methods, however, enjoy the advantage of not requiring the purchase and installation of specialized and often expensive equipment or facilities.

Two broad chemical approaches to the emulsion problem may now generally be considered:(a) preventive and (b) remedial. In the first case, if all sources of surface-active material could be prevented from finding their way into the bilge, emulsion formation could, in principle, be completely eliminated. The use of ballast tank and bilge cleaners supposedly having low emulsifying abilities such as "Clean Break" or surfactants such as "Zif" which do not appear to greatly interfere with filter coalescer efficiency would, then, form a neat closed solution to the problem. In practice, however, a variety of polar and surface-active compounds are expected to somehow find their way into the bilge. Therefore, the second case prevails and a remedial solution must be made available for the emulsified oily waste problem.

Surface-active materials capable of stabilizing emulsions may enter the bilge by (1) natural occurrence, (2) accident or (3) intention. Unfortunately, the action of most surfactants is such as to disarm the coalescer elements and render them ineffective. Surfactants may also interfere with the operation of parallel plate separators or, indeed,

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any other device which employs physical methods to enhance the separation of oil and water (5). Since schemes built on physical methods are relatively inefficient in breaking chemically-stabilized emulsions a treatment for such emulsions based on the use of chemical demulsifiers appears to be the course holding most promise.

As pointed out in the previous paragraph, such emulsions (as found in fuel tanks, storage tanks, bilge tanks, etc.) result from the presence of powerful chemical stabilizing agents. The source of these agents may range from polar compounds originating in the oils (lube oil additives, motor oil detergent additives, etc.) or waste water contaminants (protein foam and light water fire fighting fluid wash downs) to agents specifically used to routinely clean the tanks (mil spec bilge cleaners). The extraordinary stability of such emulsions is due to the formation of a highly structured interface between the continuous and discontinuous phases (6,7,8,9). Since the stability of such systems is due primarily to strong surface chemical effects, their destabilization is not likely to be easily accomplished by mechanical or physical methods as already pointed out. Such systems are best de-stabilized by chemical means especially through the use of chemical demulsifier systems which are determined to be non-specific in their demulsification action, i.e. systems which can be profitably used over a wide spectrum of chemically stabilized emulsions.

One aspect of this report, then, deals with the development and evaluation of a nonspecific chemical means for breaking emulsions in the Navy bilge waste collection and treatment system. The philosophy here, of course, is to attack problem emulsions close to their source hopefully avoiding oily waste transport to other facilities for additional treatment (10).

However, since the bilge waste collection and treatment system lacks the sophistication and controls of a well-designed shore oily waste treatment facility some rather severe real world constraints must be imposed on any chemically-based demulsification system. That is, any successful chemical demulsifier must have the following characteristics(11): (a) be unaffected by pH of oily waste, (b) be insensitive to the nature of the waste, (c) be incapable of reemulsifying the oil if excess amounts are used, (d) have high demulsifying power in the presence of particulate matter, (e) have reasonably low cost per treatment, (f) have low toxicity and (g) exhibit no dangerous behavior if inadvertently misused. Another question which must be answered is whether or not the waste oil raft is a suitable medium for the chemical demulsification technique (12). The combined capacity of the two pumps which service the donut would require approximately one hour to completely re-circulate a maximum load of 26,000 gallons of emulsified material. It is difficult to say a priori whether or not this is a suitable level of agitation to efficiently mix a candidate demulsifier with the oily waste. It is even conceivable that some sort of metering pump might be necessary to properly mix the emulsion and the demulsifier under these conditions. These considerations, then, form the basis for the search for suitable chemical demulsifier, the subject matter of this report.

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II. Experimental

A. Materials

All inorganic reagents used were ACS grade. Table 1 lists the chemical description of the commercial agents used in the tests. Emulsifiers used included Myrj 45 and Tween 85 (ICI America) and Navy Bilge Cleaner (Mil Spec C-22230A). The oil phases used included Navy Distillate (ND), Navy Turbine oil (TO) and even used motor oil (MO) drained from an automobile engine sump.

B. Laboratory Equipment and Methods

Emulsions were prepared by combining the desired quantity of emulsifier, oil and water to make a total volume of 250 ml and mixed at 13,000 RPM in a Virtis "45" homogenizer for 5 minutes. With a good emulsifier this typically produced a stable emulsion having an oil droplet size ranging from 1-5 microns. Glass test tubes were filled to 15 ml with emulsion and the demulsifier was added in varying concentration. The tubes were shaken and placed in a rack. The degree of separation was determined after 19-20 hours.

Low temperature samples were stored in a refrigerator at 4°C. Room temperature samples were stored on the bench at 22°C and high temperature samples were stored in a water bath at 45°C.

The effective demulsifier concentration was determined to be the smallest amount of demulsifier that achieved reasonable separation after 20 hours. This concentration, in general, corresponded to a break in the plot of water layer turbidity versus demulsifier concentration (see Figure 1). The turbidity was determined as follows. Five ml. samples of water were withdrawn from below the oily layer with a syringe and placed in a clean sample tube. The amount of turbidity was measured in a Klett-Summerson photoelectric calorimeter. This gave a numerical comparison between samples. An estimate of oil content in the separated water layer was accomplished by determining the turbidity produced by a known concentration of emulsified oil. Figure 2 reports this "calibration curve" and also gives ranges of turbidity which correspond to the appearance of the separated water layer in the tube.

C. Field Equipment and Methods

In the San Diego tests, a number of preliminary experiments were run in 55 gallon drums. The amount of oil ranged from 5-10%. In general, 40 gallons of emulsion were prepared. Emulsifiers included Bilge Cleaner, Superlode, Protein Foam, and Light water chemicals.

The oil, seawater and emulsifier were added to the drum and circulated with a small 30-50 gallon per minute pump until an emulsion was formed in each of the two drums (approximately 3-5 minutes). Demulsifier L (see Table 1) was then added to one drum and the results were observed.

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After 20-30 minutes samples of water were siphoned from 6 or 8"
below the surface and collected in containers to check for clarity of
the separated aqueous phase.

No laboratory was available so oil concentrations could not be
determined on a real time basis. Some samples of separated water were
added to the surface of the harbor to demonstrate that a visible sheen
of oil could not result.

Two major experiments were conducted in the new waste oil raft
(refer to Figure 3).

The raft was essentially clean at the start and contained roughly
12,000 gallons of seawater in each side.

Approximately 800 gallons of oil were added and enough Bilge cleaner,
in the first experiment, or Superlode in the second, was added to give a
concentration of approximately 0.5% emulsifier. This was circulated
with a 300 gpm pump, moving the hose around and the return hose above
the surface of the liquid, until an emulsion was formed after about 30
minutes that filled nearly all of the raft.

Demulsifier L (at 0.4% level) was then added to the emulsion while
the 300 gpm Onan pump circulated the emulsion with the outlet hose above
the surface and the inlet hose near the bottom. To get good mixing the
pump must run 45 to 60 minutes with the outlet hose moving over the
surface.

A separation time of 8-20 hours is required. Samples were removed
from the water layer with a weighted bottle that could be lowered below
the oil before the stopper was pulled.

III. Experimental Results

A. Preliminary Screening of Demulsifier/Laboratory Tests

Table 1 lists the demulsifiers and surfactants screened for
demulsification activity. The agents listed in Table 1 were screened
by carrying out preliminary demulsification tests with the 5% oil-in-
water standard emulsion containing 1% bilge cleaner as emulsifier and
using a 0.5% trial level of candidate demulsifier to test for activity.
In order to qualify for an "acceptable" rating it was necessary that
both the oil and water layers be essentially clear after a 20-hour
period. A persistent turbidity in either layer disqualified the agent
resulting in a "none" rating for overall demulsification effectiveness.
Three agents, B, D and L successfully passed the preliminary screening.
All three acceptable agents are cation-active; that is, the hydrocarbon
moiety bears a positive charge. This is the opposite case of the vast
majority of natural and synthetic surfactants (i.e. soaps and detergents)
the bulk of which are anion-active, that is the hydrocarbon-based group
bears a negative charge. Agents B and D are, chemically, dicocodimethyl
ammonium chloride.

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B. Interaction of Acceptable Agents with Various Emulsion
    Systems/Laboratory Tests

Table 2 lists the interaction of the three acceptable agents
from Table 1 with various emulsion systems which include distilled water
(DW), salt solution (1% NaCl), seawater (SW) and salt solution plus solids
(1% NaCl + 0.1% solids). In the latter case the solids were a mixture
of pumice and finely divided rust (jeweler's rouge). Most of the experi-
ments in Table 2 illustrate the effectiveness of agent L. However, a
sufficient number of experiments for agent B and D are included to
show that they are fully equivalent to agent L in their demulsification
activities. Moreover, while many experiments are listed which utilize
Navy Distillate (ND) as the oil phase several other oils are included,
i.e. dirty automobile motor oil and an additive-containing Shell turbine
oil.

The following generalized conclusions were obtained from the col-
lected data of Table 2:

(a) Oil-in-fresh water emulsions require, in addition to the demul-
sifier, a small amount of an inorganic salt to hasten separation and
clarify both the oil and water phases. The amount of added inorganic
salt required is generally no more than twice the working concentration
of the demulsifier.

(b) Oil-in-seawater emulsions are easily broken by the demulsifier
alone.

(c) Agents B, D and L are equally effective in breaking oil-in-
seawater emulsions.

(d) Emulsions containing solids were easily broken by the demul-
sifiers, the solids generally falling to the bottom of the test cylinder.

(e) Oil-in-seawater emulsions containing large amounts of oil-
soluble additives were also broken by the demulsifier; however, slightly
high demulsifier concentrations may be required in some instances.

(f) All the demulsifiers show a working range of 0.1% to 1.0%
with 0.2% considered to be a good working concentration for the majority
of laboratory-prepared emulsions.

(g) The demulsifiers are useful over a large pH range in the
presence of ionic material (soluble salts).

C. Effect of Temperature, Concentration and Solids on the Emulsion-
    Breaking Process/Laboratory Tests

Table 3 reports the influence of temperature, concentration
and solids content on demulsifier efficiency. Three types of emulsifier
at several concentrations were used to make 5% oil-in-seawater emulsions

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of Navy Distillate. The critical demulsifier concentration (see Figure 1) was studied as a function of temperature. Also reported in Table 3 are water layer turbidity readings using the Klett-Summerson photometer together with estimates of the oil content of the water layer using the calibration curve (Figure 2). Table 3 supports the generalization put forth in Table 2 and, in addition, provides the following additional observations:

(a) For a given concentration of emulsifier or detergent much less demulsifier is required at higher temperatures (45°C) than lower ones (4°C).

(b) When emulsifier concentration is increased, corresponding increases in demulsifier concentration are required for emulsion breaking.

(c) All other factors being equal the clarity of the separated water layer is much better at higher temperatures (45°C) than low ones (4°C).

(d) Emulsions containing solid particulate matter (pumice and jewelers rouge) were easily broken. Hydrophobic particles (jeweler's rouge) stayed with the oil layer; hydrophilic particles (pumice) flocculated somewhat and settled to the bottom of the water layer.

D.   Interaction of Demulsifiers Under Practical Conditions/
      San Diego Field Test

The demonstration held at the Naval Station in San Diego represented the culmination of nearly one year of laboratory tests and experiments and the opportunity to get data on the utility of selected demulsifiers under realistic field conditions. The following work plan was employed during the week of April 19, 1976, the period assigned for these tests.

Monday - Organize available equipment and meet personnel and discuss oily waste treatment problems.

Tuesday - Preliminary mixing experiments to establish working parameters.

Wednesday - Waste Oil Raft experiments and supplementary experiments in 55 gallon drums.

Thursday - Demulsification tests in specific problem areas at the San Diego facility, i.e. emulsions caused by Light Water chemicals, Protein Foam, Mil Spec Bilge Cleaner, Superlode Degreaser, etc.

Friday - Field demonstration; discussion of test with interested Navy personnel.

Table 4 reports the results of the five day tests in concise summary form. In general, the field tests bore out the laboratory experiments. The geometry of the test container whether drum, WOR or OR vessel was not important <u>provided mixing of demulsifier with oily waste was adequate and of sufficient duration</u>. In the case of the WOR, for example, orientation of the mixing hoses used with the 300 gpm Onan pump is crucial to good mixing as previously mentioned in the experimental section (see Figure 3). One hour should be allowed for thorough mixing when a 300 gpm pump is used.

E.   Vapor Pressure Osmometry Experiments

A limited basic study was made of several agents in their dispersed forms in water and in heptane. Two pieces of information were desired:

(1)   the molecular weight of Agent "L", and

(2)   the physico-chemical state of the dispersed phase of these agents.

Figure 4 is a calibration curve of the standardizing solute in acetone taken in the Mechrolab vapor pressure osmometer. Several solutes were used for calibration including ethylene glycol, benzil and even a vacuum-dried dicocodimethylammonium chloride sample. A calibration constant of 582 ohm-liter-mole^{-1} was obtained for acetone solutions. Figure 5 shows the results obtained for acetone solutions of Agent L. An intercept value of 0.715 ohm-liter-gram^{-1} was obtained which when combined with the calibration constant yielded a molecular weight of 814. Agent L has nearly double the molecular weight of Agents B and D. Since agent L is also a quaternary ammonium chloride it might be conjectured that its structure may possibly be:

$$CH_3 \; (CH_2)_{12.6} \quad _4 \quad N^+Cl^-$$
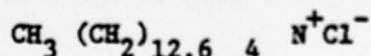
or essentially tetracocoammoniumchloride. An alternative structure (though less likely) might be

$$CH_3 \; (CH_2)_{25.1} \quad _2 \; (CH_3)_2 \; N^+Cl^-$$
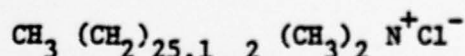
The physical chemical state of emulsifiers and demulsifiers in solution may also have some bearing on their efficiencies or effects.

Figures 6-8 report the vapor pressure osmometry of Tween 85 (a relatively discreet emulsifier) and dicocodimethylammoniumchloride (a demulsifier) in terms of instrument resistance versus concentration. Figure 6 shows the data obtained which allowed estimates of the tendency of these substances to aggregate in water and heptane. Heptane

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simulates the solvent properties of Navy Distillate fuel oil (since ND cannot be used in vapor pressure osmometry (PVO) because of its low volatility). That emulsifiers and demulsifiers form aggregates or micelles in water is shown by their early departure from the sodium chloride calibration curve. These curves allow estimates of average micelle size, $(\bar{n})$, and critical micelle concentration, (CMC).

In heptane, however, (see Figures 7 and 8) the emulsifier and demulsifier show somewhat different effects. While the CMC's of Tween 85 and dicocodimethylammonium chloride are respectively 2.5×10^{-4} m/l and 5×10^{-4} m/l in water their departure from the biphenyl calibrating curve in heptane differ from each other by more than an order of magnitude in concentration. Thus it can be shown that the emulsifier is a very weak micelle-former in heptane. Figure 9 and Table 5 summarize the data more succinctly in both tabular and graphical form.

Mixtures of Tween 85 and dicocodimethylammonium chloride were also studied to determine whether or not any significant interactions took place between good emulsifiers and good demulsifiers in either the continuous or dispersed phases, i.e. cooperative micelle formation, etc. Table 6 lists the observed vapor pressure lowering in terms of thermistor resistance and the predicted vapor pressure lowering for selected mixtures of the two agents in both water and heptane.

The VPO results show that:

(1) Tween 85 is a good micelle-former in water ($\bar{n} = 7$) but poor in heptane ($\bar{n} = 2$)

(2) Dicocodimethylammonium chloride can form large micelles both in water ($\bar{n} > 37$ in ultimate size) and in heptane ($\bar{n} > 16$).

(3) The data are not indicative of any significant interactions between agents in either solvent.

These experimental results are consistent with previous concepts advanced on the mechanism of emulsifier-demulsifier displacement and film weakening (6,7,8).

IV. Discussion

A. Introductory Statement

To the present day no single coherent theory of emulsion formation and stability exists. Moreover, little is also known about the mechanism of demulsification, especially as triggered by the addition of certain active agents (demulsifiers). The work done in this report relies heavily on a combination of intuition, trial and error together with a touch of serendipity. While a useful class of demulsifiers seems to be established by this work it must be emphasized that empirical research is not a substitute for basic knowledge. Basic knowledge can

greatly reduce the number of trial and error experiments and allow a
greater control of processes. Lesser degrees of knowledge subject us
to the whims of nature (and man) which subsequently result in crash
programs to solve emergency situations as control of the process breaks
down. Section B and C of the discussion section partially summarize
basic concepts in emulsification and demulsification.

B.   Theory of Emulsification

A proper theory of emulsions (3) must explain the following
important behavioral characteristics: (a) formation, (b) stability,
(c) demulsification, (d) chemical factors, (e) physical factors. These
factors will now be considered separately in abbreviated form.

1.   Emulsion Formation

Surfaces contain an energy over and above other forms of intrinsic
energy already present. Therefore, to create additional surface, energy
must be supplied to the system in proportion to the area created. In
the case of oil-water systems, the equation

$$\Delta F = -W_{max} = \int_{A_1}^{A_2} \tau_{o/w} dA$$

describes the process where ΔF or $-W_{max}$ represent the energy requirement,
$\tau_{o/w}$ is the interfacial tension between the oil and water, and A refers
to the area. It is clear that the work required to form an emulsion will
be reduced when surface-active agents are added to the system. For
example, the interfacial tension between pure water and an oil will
typically be of the order of

$$\tau_w - \tau_o = 72 - 30 = 42 \text{ dynes/cm}$$

Therefore, the addition of a surface-active agent to the system may
reduce the interfacial tension to something of the order of say
2 dynes (depending on concentration, type of surfactant, etc.). Thus,
the new energy requirement to produce the given surface area in the
presence of surfactant is only 5% of its former value. Any forces
which can produce movement of one phase with respect to the other may
easily supply this lowered energy. It should be pointed out, however,
that though the emulsion may be easily produced as a result of the
lowered interfacial tension it is not necessarily stable. The physical
properties of the material at the interface control the stability of the
emulsion (3,4).

2. Emulsion Stability

The stability of an emulsion is directly related to the nature of the interfacial film at the interface between dispersed drops and the continuous phase. Three distinct classes of stabilizing interfacial films are recognized: (a) solids, (b) protective films (such as hydro-philic colloids and polymers) and (c) surface-active agents. One would expect that an emulsion would be highly stable if the interfacial film had good mechanical strength and this turns out to be precisely the case. In case (a), finely divided solids which are incompletely wetted by both the water and oil will tend to collect in the interface forming mechanically tough films. Cases (b) and (c) also result from the appearance of a tough adsorbed layer at the interface. The adsorption of soluble agents at the interface, however, is governed by the Gibbs adsorption isotherm which in approximate form is:

$$\Gamma_2 = \frac{c}{RT} \left(\frac{\partial \tau}{\partial c}\right)_T$$

where Γ_2 is the concentration of agent at the interface, C is the concentration of agent in the bulk solution (continuous phase), T is the absolute temperature and R is the gas constant. After or during adsorption at the interface other events may take place which may further strengthen the toughness of the film. For example, a polymer may set to a mechanically rigid gel in this interfacial layer or a soap may interact with both water and oil to form a rigid liquid-crystalline layer (9). Other effects contributing to emulsion stability may take place as the complexity or number of components in both the oil and water phases increases. Of special note is the additional stability offered by the appearance of electric charges at the oil-water interface and the resultant repulsive force between drops bearing similar charges (3).

C. Theory of Demulsification

Separation of the disperse phase occurs as a two step process. In the first stage the dispersed droplets flocculate, that is, the droplets cluster together forming aggregates of droplets. In the second stage the aggregated droplets coalesce to form a single drop. While the first stage is reversible the second one is not and the number of oil droplets decreases in the system ultimately leading to complete demulsification as the process continues to its conclusion. Since demulsification is a two step process the overall rate of emulsion-breaking will depend on whether the rate of flocculation or the rate of coalescence is the slowest rate. In dilute emulsions the rate of flocculation is smaller than the rate of coalescence, and hence is rate-determining. In highly concentrated emulsions the reverse is true, i.e. the rate of coalescence determines the rate of demulsification. In emulsions of intermediate strength the rates of both processes will be of the same order of magnitude. These statements may be given a somewhat

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mathematical formulation by invoking Smoluchowski theory (13) and employing several useful modifications and approximations introduced by Van den Tempel (14, 15).

The total number of droplets whether flocculated or not, in an emulsion undergoing separation is found by adding the number of un-reacted primary droplets to the number of droplets contained in the aggregates, that is:

$$N = n_1 + n_v m$$

$$= \frac{n_o}{1 + an_o t} + \frac{an_o^2 t}{(1 + an_o t)^2} \left[\frac{an_o}{K} + (1 - \frac{an_o}{K}) e^{-Kt} \right]$$

where n = total number of droplets

n_1 = total number of primary droplets at time t

n_v = number of aggregates

m = number of droplets per aggregate

n_o = initial number of droplets at t=0

t = time

a = constant $\doteq \frac{4Kt}{3\eta}$ or $\sim 10^{-11}$ cm^{3}sec^{-1}

K = a measure of the rate of coalescence

For a dilute emulsion,

$$\frac{an_o}{K} \ll 1$$

and the modified Smoluchowski equation reduces to

$$n = \frac{n_o}{(1 + an_o t)}$$

For a concentrated emulsion,

$$\frac{an_o}{K} \gg 1$$

and the modified Smoluchowski equation reduces to

$$n = \frac{n_o}{Kt} (1 - e^{-Kt})$$

While these equations express the _kinetics_ of emulsion-breaking or

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demulsification they do not yield any information whatsoever on the kinds of processes by which flocculation and coalescence take place, i.e. those critical changes in the nature of the interfacial film which reduce the barriers to flocculation and coalescence. It has long been thought (3,4) that the strength, compactness and elasticity cf the interfacial film are the most important factors favoring emulsion stability. Recent work (8) examining interfacial films in water/crude oil emulsions through measurements of interfacial tension, interfacial viscosity and interfacial film pressure-film area measurements support that view in a most elegant fashion.

Demulsifiers, then, may act in two ways. First, they may modify and weaken the interfacial film allowing flocculation and coalescence to take place although not necessarily at optimum or acceptable rates. Second, they may cause disintegration of the layer by destroying the structural-mechanical properties of the interfacial film. In the process of demulsification the following processes may take place individually or concurrently (6):

1. Displacement of the stabilizing agent from the interface by the demulsifier which forms very weak interfacial films at best.

2. Removal of stabilizing particulate matter from the interface through coagulative action and/or wetting of the particles by either of the liquid phases.

3. Solubilization of residual stabilizing material in the oil and/or water by surfactant (demulsifier) micelle or molecules.

4. Suppression of re-emulsification through use of a demulsifying agent that can form micelles in both aqueous and organic phases (limits concentration of free soap monomer).

5. Flocculation of droplets.

6. Coalescence of droplets to form drops.

7. Sedimentation of drops leading to separation of bulk phases.

D. A New Approach to Emulsion Stability and Demulsification (Chemical Factors)

Presumably, if the factors involved in emulsion stabilization are known with any degree of certainty, a strategy can be devised by which such emulsions can be conveniently demulsified. In order to understand emulsification and the opposite process of demulsification, one must have meaningful information on the components involved in the emulsification process; specifically water, oil and agent (1). Of the three components only water is invariant. In other words, the nature of both the oil and the stabilizing agent may vary considerably. Nonetheless, it is strongly suspected but not yet thoroughly documented that

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the most effective agent to be used in stabilizing an emulsion will be dictated to a certain extent by the nature of the oil phase.

In order to understand the emulsification process it is useful to employ some scheme of rating the components involved. In the case of the stabilizing agent a numerical scale, the so-called HLB system (17) exists. HLB stands for the hydrophilic-lipophilic balance of the emulsifier molecule and is determined through a series of experimental emulsion tests for each agent. Table 7 gives an idea of surfactant function versus HLB value and puts forth the point that the type of emulsion formed will be a function of the surfactant HLB. However, the optimum HLB to produce W/O or O/W emulsions appears to systematically vary with oil type - a point which seems to have been missed by workers in this field. Figure 10 introduces a new factor which indexes oil type - the solubility parameter or the square root of the cohesive energy density of a given substance (18). It is a measure of inter-molecular attractive forces and is defined as $\delta = (\frac{\Delta E}{V})^{1/2}$ where ΔE is the energy of vaporization and V is the molar volume.

Figure 10 emphasizes that the optimum HLB for a given surfactant to emulsify an oil will be dictated by the solubility parameter of the oil. Where the attractive forces between oil molecules are low, as in the case of silicones, the stabilizing agent should have a value of 11 for the optimum effect. For benzene, where the intermolecular forces are higher, the optimum HLB is 4 units greater. It is now possible to assign numerical indices to both components of the emulsion which are expected to be variable, i.e. solubility parameter for the oil and HLB number for the surfactant. Moreover, an additional clue has been provided for these basic studies in that the type of oil used - as indexed by its solubility parameter - will dictate the required HLB of the surfactant for optimum emulsion stability.

Much the same view can be obtained from semi-theoretical considerations. Ignoring, at least momentarily, the complications of polarity one may combine the definition for the solubility of substances which form regular solutions with Davies' relation between HLB and the relative solubility of the surfactant between oil and water phases. If this is done one obtains:

$$HLB-7 = \frac{0.36 \, V_s}{RT} \left[\phi_{II}^2 \, (\delta_{II} - \delta_s)^2 - \phi_I^2 \, (\delta_I - \delta_s)^2 \right]$$

where V_s = molar volume of surfactant

    R = gas constant

    T = absolute temperature

    ϕ = volume fraction

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δ = solubility parameter

I = aqueous phase

II = oil phase

s = surfactant

Since δ_I is fixed and the volume fraction of each phase is usually close to unity it is obvious that there is for each particular oil-water system a unique value of δ_s (or HLB) for the surfactant which will be determined by the δ_{II} value characterizing the oil. Such a view, from a different basis, has also been reported in the literature. In this work, plots of HLB versus the ratio of the chemical potentials of surfactants in the standard state in oil and water have two distinct linear relations for the isooctane-water and benzene-water systems.

It is felt that these considerations may provide the basis for meaningful research on the stabilization of emulsions by surface-active materials. With the nature of the oil and the surfactant numerically indexed one important factor remains – the structure or nature of the interfacial film. One relatively recent theory suggests that emulsion stability results from the formation of liquid crystal interfacial films (16). Liquid crystalline films particularly of the smectic type can be expected to be highly viscous or even semi-solid. Therefore, one can readily rationalize the stability of particularly stubborn emulsions as perhaps due to the appearance of such films. The possibility of liquid crystalline development is established by a phase diagram study of the particular system of interest. Thus, another rating system suggests itself – the viscous or solid-like characteristics of the interfacial film as deduced from measurements in the bounded liquid-crystalline region derived from the phase diagram studied.

The stability of emulsions, then, will be indexed by three factors – surfactant HLB, oil solubility parameter and viscosity or yield stress of the liquid crystalline phase. This at least provides an initial plan to characterize emulsion stability. Demulsification agents are also surface-active in nature and may also be rated by the HLB system. The interaction of demulsifiers with such characterized emulsion systems may, then, also be numerically indexed and classified. It is expected that rules for the demulsification of oil-water systems of any type might develop out of these considerations and that a basis would be provided by which emulsion problems in critical Navy functions might be quickly solved through the employment of guidelines arising out of such fundamental studies. Research Proposal No. II in the Appendix section specifically addresses this problem.

E. Practical Demulsification

The ideal chemical demulsifier for oil-in-water emulsions should, in general, possess the following characteristics as already

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mentioned in the Introduction:

(1) Be unaffected by pH of oily waste

(2) Be insensitive to the nature of the oily waste

(3) Be incapable of re-emulsifying oil if excess amounts are used

(4) Have high demulsifying power in presence of particulate matter

(5) Have low cost per treatment

(6) Have low toxicity

A demulsifier which meets all of these qualifications has not been found. The practical demulsifier must be a compromise demulsifier in which the above requirements are at least partially met. Within the experimental designs of the empirical laboratory testing done so far, characteristics (1), (2), (3) and (4) have been met by agents B, D and L (see Tables 2 and 3). Items (5) and (6), however, bear further discussion and it may be worthwhile to discuss these in some detail. It should be noted that water-in-oil emulsions require separate treatment.

1. Organic vs. Inorganic Emulsion-Breakers

The use of organic vs. inorganic (acids, alum, ferric chloride, etc.) emulsion-breakers is of vital concern in the economics of and efficiencies desired in oil-water separation technology. The physical treatment of oil droplets which have coalesced to diameters of the order of 40-50 micrometers through the action of an appropriate demulsifier may be accomplished by either gravity or air flotation methods. In either case Stokes' Law applies:

$$V = \frac{d^2 \Delta\rho g}{\mu}$$

where V = rise rate

d = diameter of droplet

g = gravitational constant

$\Delta\rho$ = density difference between phases

μ = viscosity of continuous phase

In the case of air flotation the effective diameter is greater and the density difference between phases is increased due to the bubbles of air attached to the oil droplet greatly increasing the rise rate. Inorganic chemicals function by neutralizing the charge on oil droplets

and also producing a large amount of surface (voluminous precipitates) which aids in the entrapment of oil droplets. However, a bulky sludge is produced which further complicates the handling or disposal problem. Moreover, the dissolved solids are increased in the waste stream. While the use of floc-forming inorganic demulsifiers adds a degree of awkwardness to the use of gravity separation or air flotation systems, such chemicals would be disasterous if employed with filter coalescer systems.

Organic demulsifiers, on the other hand, do not interfere with gravity separation and air flotation systems; they may also be a useful complement to filter coalescer oil separation technology, although this is a matter requiring additional research. If organic chemical demulsifiers can be added to waste oil rafts and if they do not interfere with coalescer or parallel plate separation action, then the overnight settling time prescribed by the laboratory and field tests of this report may even be reduced to an hour or so followed by pumping the treated emulsion through either the filter coalescer or parallel plate separator.

2. Demulsifier Costs

In order to visualize operating costs it is useful to consider the most extreme case which might be encountered - that of a fully fouled donut containing 26,000 gallons of emulsion. Laboratory and field tests suggest a range of 0.2% to 0.6% demulsifier at temperatures of 60° to 80°F together with an overnight period (∿ 14 hours) for oil-water separation. Demulsifier levels can be decreased (see Table 8) when higher temperatures are used. On the other hand, emulsions at lower temperatures, as near the freezing point of water, require substantially more demulsifier to be successfully broken. Table 8 summarizes estimated costs of treatment for 26,000 gallons of emulsion. Demulsifier costs can be reduced by thorough irrigation of the emulsion with sea water. Some bilge emulsions may depend in part on low salinity for their stability. A recent sample (19) received from the USS Hurley seems to bare this out. An increase in salinity brought about by mixing equal parts of emulsion and sea water sufficed to break the emulsion although the water layer was somewhat hazy (20). Addition of demulsifier and sea water together promoted a very clear water layer. With regard to the time required for separation it is conceivable that the addition of demulsifier will sufficiently reduce the stability of the emulsion so that the treated emulsion could be immediately run through the parallel plate separator or filter coalescer thus saving much time. It is also conceivable that the action of parallel plate separators and filter coalescers may be such as to reduce the amounts of demulsifier needed to much lower levels than the NRL experiments and field tests have indicated (12).

3. Toxicity of Candidate Demulsifiers

Some idea of the toxicity of some selected emulsifiers and demulsifiers is given in Table 9. The data in the table is taken from

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references 21 and 22. The toxicity of Agent L is not known, no information being available from the manufacturer, but it is probably no more toxic than Agents B and D since its molecular weight is considerably higher (toxicity decreases with molecular weight due probably to the decreased solubility in the aqueous phase). Agents B and D might be classified as practically nontoxic although they perhaps would not qualify for food additive use as do the Span and Tween compounds. The oral LD_{50} data were derived from tests on rats with the exception of Tween 20 which used hamsters as test subjects. This preliminary view of the candidate demulsifiers suggests that there should be a minimum of concern over the use of these compounds in this application.

4. Decision-Making Process on Use of Demulsifiers

When a waste oil raft arrives at dockside full of emulsion a decision will have to be made as soon as possible on the treatment or transport of the oily waste. Figure 11 identifies, in a somewhat simplified manner, some salient features of this decision-making process. Critical to this schematic are the development of tests upon which to base the required decisions. Two tests, one for emulsion type and one for salinity, are necessary for the implementation of this logic diagram. They will now be briefly outlined.

(a) Test for Emulsion Type

(1) Take two clear tubes or bottles

(2) Add clean water to one tube and clean (preferably clear) fuel to the other.

(3) Add emulsion to each tube and stir very gently (no need to shake)

Observations

(1) If the emulsion easily mixes with water but does not mix with the fuel (i.e. there are two layers) then the emulsion is oil-in-water (O/W).

(2) If the emulsion easily mixes with fuel but does not mix with water (two layers) then the emulsion is water-in-oil (W/O).

(b) Test for Salinity

A Conductivity Salinity meter is available from Fisher Scientific Co., Model 33 (YSI 33). Its cost is $195.00 and it reads percentage of salt directly. Fresh water would read close to 0% and sea water approximately 3%.

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5. Preliminary Suggestions for a Chemical Treatment Procedure

When donut is full of emulsion, oil will be detected in the observation well. The following procedure applies:

A. Stop flow into donut and close effluent valve.

B. Pump all separated oil from both primary and secondary sites of donut.

If the emulsion does not break the chemical separation method can be used as follows:

(1) Start mixing the primary side of donut with a 300 gpm or larger pump using a hose to pump near the bottom of donut and an outlet hose at the surface.

(2) Add approximately 0.2% demulsifier at a rate of 3-5 gpm (about 1/2 drum per 12,000 gallons) at surface of primary side with stream from the mixing pump.

(3) Continue mixing 60 minutes after demulsifier has been added.

(4) Withdraw a sample from 2 or 3 feet below surface then turn off pump and allow emulsion to separate (8-20 hours). If emulsion does not break (observe sample bottle) repeat steps 1-3; otherwise proceed to steps 5 and 6.

(5) After separation remove oil from both sides of donut. (This operation will add more sea water to secondary side of donut and should achieve separation there while the primary side is being treated with chemicals.)

(6) If separation is not complete in secondary side of donut it can be treated the same way as the primary side with additional demulsifier.

6. Breaking Water-in-Oil Emulsions

(a) Background

A new chemical demulsifier system has been developed at NRL (6) which shows potential for solving a problem which has caused the Navy great difficulty for many years. This new demulsifier, if it can be applied practically, should permit separation of water from stubborn water-in-oil emulsions prior to entry into shipboard fuel-supply systems for the main propulsion plant.

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The NRL demulsifier system has proved itself in laboratory tests to be more effective than commercially available agents in breaking up these water-in-oil emulsions. The new demulsifier is really a two-part system, comprising an effective wetting agent (sodium dioctyl sulfosuccinate) and a high-molecular-weight polymer (polyethylene oxide). It is so effective that even stiff, buttery emulsions are thinned and broken at temperatures as low as 50°F. Most commercial demulsifiers, on the other hand, require that the emulsion be heated to well above 100°F to realize their full effectiveness. Tests have shown the new demulsifier to be quite effective, even with stable water-in-oil emulsions containing large amounts of dirt, rust, and other particulate matter. An example of the effectiveness of the demulsifier is shown in Figure 12 where the demulsification of an extremely stable 50% water-in-oil emulsion (using 10% NSFO in ND as the oil phase) is illustrated at 50°F. Demulsification is essentially complete in 15 minutes.

(b) Preliminary Procedure for Breaking Water-in-Oil Emulsions with NRL Demulsifier

Since this procedure involves a two part demulsifier and may involve re-emulsification if excess amounts are used, emulsion treatment is best left to trained personnel at any appropriate oily waste treatment plant.

Procedure

The amount of demulsifier to be used will be dependent upon a number of variables such as emulsifier type and concentration, salinity, temperature, water content, and solids content. A rule-of-thumb procedure is as follows:

(1) Mix in surfactant (75% aq. solution as supplied) to make a 0.05% solution based on the estimated water content of the emulsion.

(2) Add 0.5% aq. Polyox FRA to make a 0.005% solution (also based on estimated water content).

(3) After thorough mixing, take emulsion sample and allow to stand in a graduate or transparent cylinder for at least 5 minutes. Note the rate of emulsion breaking.

(4) If no breaking observed or if breaking is too slow (only 10% of emulsified water has separated) then add same quantities of agents as in steps (1) and (2) and observe emulsion as in step (3).

(5) Repeat steps (1) and (4) until emulsion is easily broken as indicated by about 50% of the emulsified water separating within 5-10 minutes in the sample cylinder.

(6) Stop agitation and allow emulsion to separate for 30 minutes.

Notes

(a) If excess demulsifier is added the w/o emulsion will invert to o/w.

(b) The first additions of Aerosol OT cause the thick emulsion to become quite fluid when properly mixed-in.

(c) As the optimum amount of demulsifier is approached there is a significant darkening of the stirred emulsion surface as the oil begins to separate.

(d) Success depends upon thorough mixing of demulsifier with the emulsion.

V. Conclusions and Recommendations

A. The laboratory and field work of this report support the following broad overall conclusions:

1. A class of cationic demulsifiers has been identified which approximately conform to the requirements listed under item E of the Discussion section.

2. The waste oil raft is an acceptable vehicle for oil-in-water emulsion breaking operations *provided* mixing methods for the demulsifier are adequate.

B. The following recommendations are made:

1. A pilot study of demulsifier effectiveness (for oil-in-water emulsions) in waste oil rafts should be made to gain the widest possible field experience on the use of these cationic agents.

2. A field test in a Ship Waste Offloading Barge (SWOB) may be in order. While the SWOB lacks the flexibility of the WOR its shortcomings may conceivably be overcome with an appropriate combination of demulsifier and inorganic salts.

3. The use of these cationic agents in shore-based oily waste treatment plants should also be considered, especially since they apparently serve as emulsion-breakers and water-clarification aids (especially against negatively charged sediments such as clays, etc.)

4. The economics of chemical demulsification should be optimized as follows: (a) by extracting and recycling agents recovered from the broken emulsion system and (b) by more efficient use of presently available agents and the development of improved demulsifying agents or systems. The two proposals of the Appendix section address these considerations.

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Table 1

Demulsifier Agents Investigated

Agent	Chemical Description	20-hour Demulsification Activity (Room Temperature)
A	Cocotrimethylammonium Chloride	None
B	Dicocodimethylammonium Chloride	Acceptable
C	N Tallow pentamethyl propane diammonium dichloride	None
D	Dicocodimethylammonium Chloride	Acceptable
E	Proprietary surfactant	None
F	Proprietary surfactant	None
G	Polyelectrolyte blend	None
H	Mixed Mono and Dialkyl Quaternary Ammonium Chlorides, Average Mol. Wt. = 394	None
I	Organic compound of polymeric type	None
J	Proprietary surfactant	None
K	Cationic surfactant	None
L	Modified quaternary ammonium compound	Acceptable
M	Polymeric Amine Liquid	None
N	Polymeric Amine Liquid	None
O	Polymeric Amine Liquid	None
P	Polymeric Amine Liquid	None
Q	Cationic Amine Liquid	None
R	Cationic Quaternary Amine Liquid	None
S	Cationic Quaternary Amine Liquid	None
T	Sodium dioctylsulfosuccinate	None
U	Alkylamine-quanidine polyoxyethanol (cationic)	None
V	Antifoam Additive; fatty alcohol?	None
W	Quaternary Ammonium Compound	None
X	Quaternary Ammonium Compound	None
Y	Polyoxyethylene-Polyoxypropylene Copolymer MW=2000	None
Z	Polyoxyethylene-Polyoxypropylene Copolymer MW=2500	None
AA	Polyoxyethylene-Polyoxypropylene Copolymer MW=3800	None

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Table 2

Demulsifier Interactions with Various Oil-Water Systems

Demulsifier	Oil Type	Oil Conc.	Aqueous Medium	Bilge Cleaner Conc.	Demul. Conc. Required	Inorganic Salt	Inorganic Salt Conc.	Time Required for Separation	Appearance of Water Layer
Agent "L"	ND	50%	DW	0.5%	0.5%	K_2CO_3	0.2%	5 min.	Clear
"	ND	50%	1% NaCl	0.5%	1.0%	K_2CO_3	0.1%	15 min.	Clear
"	ND	50%	1% NaCl	0.5%	0.2%	K_2CO_3	0.8%	5 min.	Clear
"	ND	50%	1% NaCl	1.0%	0.2%	K_2CO_3	0.5%	5 min.	Clear
"	ND	50%	DW	0.1%	0.2%	K_2CO_3	0.4%	Overnight	Clear
"	ND	50%	DW	1.0%	0.4%	K_2CO_3	1.0%	6 min.	Clear
"	ND	50%	DW	0.5%	0.5%	K_2SO_4	1%,pH=2	Overnight	Clear
"	ND	50%	DW	0.5%	0.5%	K_2SO_4	1%,pH=7	Overnight	75% sep.
"	ND	50%	DW	0.5%	0.5%	K_2SO_4	1%,pH=10	Overnight	Clear
"	ND	5%	DW	0.5%	0.3%	K_2CO_3	0.2%	Overnight	Clear
"	ND	5%	DW	0.5%	0.1%	K_2CO_3	0.6%	10 min.	Clear
"	ND	50%	DW	0.5%	0.2%	K_2CO_3	0.6%	Overnight	Cloudy
"	ND	5%	1% NaCl	0.5%	0.2%	K_2CO_3	0.1%	Overnight	Cloudy
"	ND	5%	1% NaCl	0.5%	1.0%	K_2CO_3	0.2%	Overnight	Clear

Table 2 (Continued)

Demulsifier	Oil Type	Oil Conc.	Aqueous Medium	Bilge Cleaner Conc.	Demul. Conc. Required	Inorganic Salt	Inorganic Salt Conc.	Time Required for Separation	Appearance of Water Layer
Agent "L"	ND	5%	SW	0.5%	0.2%	-	-	Overnight	Clear
"	ND	5%	1% NaCl	0.5%	0.5%	K_2CO_3	0.6%	Overnight	Clear
"	ND	5%	SW	0.5%	0.2%	-	-	Overnight	Clear
"	ND	5%	1% NaCl+ 0.1 solids	0.5%	0.2%	-	-	Overnight	Clear
"	MO	5%	1% NaCl	1.0%	0.6%	K_2CO_3	1.0%	Overnight	Clear
"	TO	5%	SW-DW	1.0%	0.5%	-	-	Overnight	Clear
Agent "D"	ND	5%	SW	0.5%	1.0%	-	-	Overnight	Clear
"	ND	5%	SW	0.5%	0.15%	-	-	Overnight	Clear
"	ND	5%	SW	0.5%	0.2%	-	-	Overnight	Cloudy
"	ND	5%	DW	0.5%	0.3%	K_2CO_3	0.2%	Overnight	Clear
"	ND	5%	DW	0.5%	0.2%	K_2CO_3	0.5%	Overnight	Clear
Agent "B"	ND	5%	SW	0.5%	0.5%	-	-	Overnight	Clear
"	ND	5%	SW	0.5%	1.0%	-	-	Overnight	Clear

ND - Navy Distillate
MO - Used Motor Oil
TO - Shell Turbine Oil

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Table 3

Effect of Temperature, Concentration and Solids in the Emulsion - Breaking Process

Critical Demulsifier Concentration, Turbidity and Estimated Oil

Emulsifier	Solids Content	Emuls. Conc.	Demulsifier	4°C			24°C			45°C		
				CDC	Turb[1]	Oil[2]	CDC	Turb.	Oil	CDC	Turb.	Oil
Myrj 45	0	0.2%	Dicocodimethylammonium Chloride (DCDMAC)	0.8%	170	250 ppm	0.8%	31	32 ppm	< 0.1%	10	9 ppm
Myrj 45	0	1.0%	"	--	--	--	1.0%	135	190 ppm	--	--	--
Tween 85	0	0.1%	"	0.8%	230	380 ppm	0.2%	125	170 ppm	0.05%	0	0 ppm+
Tween 85	0	1.0%	"	∿1.5%	270	480 ppm	1.2%	58				
Bilge cleaner	0	1.0%	"	0.6%	61	74 ppm	0.2%	38	42 ppm	0.1%	24	24 ppm+
Bilge cleaner	0	5.0%	"	2.0%	87	115 ppm	0.6%	52	60 ppm	0.5%	33	34 ppm
Tween 85	0	0.1%	Mod.Quat.Amm. Cpd.(MQAC)	0.5%	80	100 ppm	0.2%	20	19 ppm	0.05%	19	19 ppm+
Bilge cleaner	0	1.0%	"	0.7%	300	520 ppm	0.5%	240	400 ppm	0.4%	49	55 ppm+
Tween 85	0.05% clay 0.05% Fe_2O_3	0.1%	DCDMAC	0.6%	120	--	0.25%	125	--	0.1%	73	--
Tween 85	"	0.1%	MQAC	0.4%	530	--	0.15%	149	--	0.2%	53	--
Bilge cleaner	"	1.0%	MQAC	1.0%	170	--	0.7%	160	--	0.2%	58	--
Bilge cleaner	"	1.0%	DCDMAC	0.8%	180	--	0.2%	32	--	0.1%	25	--

Appearance Turbidity Readings - Clear = 0 → 10; slightly hazy = 10 → 50: Hazy = 50 → 300; Cloudy = 300 → 900; Turbid = > 900

(1) arbitrary Klett Summerson instrument readings; (2) estimated from calibration curve of instrument response to emulsions of known oil content

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Table 4

Summary of San Diego Field Tests

Run #	Test Geometry	Emulsifier	Manuf.	Emuls. Conc.	Oil Phase	Demuls. Conc.	Remarks
1	55 gal.	M.S. Bilge Cleaner	Phipps	0.6%	waste fuel mix	0.6%	Bulk of oil separated after 15 min; water layer cloudy but cleared overnight.
2	drum					control	No separation observed; emulsion stable.
3	55 gal.	Superlode degreaser	West Chemical Products	0.6%	used Navy motor oil	0.6%	Good separation after 10 min; water hazy but cleared overnight.
4	drum					control	Slight separation of oil overnight; bulk of oil remained emulsified
5	55 gal.	AFFF fire fighting fluid	3M	0.6%	waste fuel	0.6%	Emulsion broke easily within 3 or 4 min; water layer hazy.
6	drum					control	Emulsion breaks spontaneously over course of several hours; water layer very cloudy.
7	WOR	M.S. Bilge Cleaner	Phipps	0.3%	waste fuel	0.3%	Results confirm drum experiment (Run #1).
8						control	Water layer cloudy, same as Run #2.

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Run #	Test Geometry	Emulsifier	Manuf.	Emuls. Conc.	Oil Phase	Demuls. Conc.	Remarks
9	55 gal. drum	M.S. Protein fire fighting fluid	Mearl Corp.	0.5%	waste fuel	0.3%	Emulsion broken after about 10 min; water layer cloudy.
10	drum					control	Emulsion slowly separates over period of several hours, water layer very cloudy.
11	oil recovery boat tank	unknown but contains paint plus motor oil additives	--	--	mixed oils, engine oils, fuel oils,etc.	0.8%	Emulsion was inverse type, i.e. water-in-oil. Demulsification generally useful only for oil-in-water types but raising demulsifier concentration to 0.8% broke emulsion overnight.
12	55 gal. drum	Superlode degreaser	West Chemical Products	0.3%	waste fuel	0.2%	Same as Run #3 but emulsion was concentrated, i.e. was ~ 50% oil-in-water rather than 5% oil-in-water as in other experiments.
13	WOR	Superlode degreaser	West Chemical Products	0.3%	waste fuel.	0.2%	Results similar to Run #7 but emulsion was concentrated, i.e. 50% oil-in-water. Water layer hazy but cleared overnight.

Table 5

Aggregation Data for Agents in Water and Heptane

Compound	Solvent	Conc'n (moles/1)	$\bar{m}$	Conc'n	$\bar{m}$	Conc'n	$\bar{m}$	Conc'n	$\bar{m}$	Conc'n	$\bar{m}$	CMC (m/1)
Tween 85	Heptane	0.0218	1.10	0.0436	1.30	0.0873	1.89	0.131	2.03	0.218	1.97	1.85×10^{-2}
Dicoco-dimethyl-ammonium chloride	Heptane	0.00339	~9	0.0136	13	0.0237	14	0.0339	16			4×10^{-4}
Tween 85	Water	0.000484	2.6	0.00242	3.2	0.012	9.5	0.0303	7.4	0.0453	6.4	2.5×10^{-4}
Dicoco-dimethyl-ammonium chloride	Water	0.000456	1.2	0.00228	4.6	0.0114	17.5	0.0228	26	0.0570	37	5×10^{-4}

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Table 6

Mixtures of Tween 85 and Dicocodimethylammonium chloride

Solvent	Molarity		Predicted ΔR	Observed ΔRX
	Tween 85	Dicocodimethyl- ammonium chloride		
Water	3.02×10^{-2}	5.07×10^{-2}	0.90	1.03
	1.51×10^{-2}	2.58×10^{-2}	0.49	0.60
	7.5×10^{-3}	1.29×10^{-2}	0.34	0.30
	3.8×10^{-3}	6.4×10^{-3}	0.25	0.14
Heptane	4.36×10^{-2}	1.70×10^{-2}	11.66	11.33
	1.09×10^{-2}	1.70×10^{-2}	4.73	4.60

Table 7

Surfactant Function vs. HLB Value

HLB Range	Application
1 – 6	W/O emulsifier
7 – 9	Wetting agent
8 – 18	O/W emulsifier
13 – 15	detergent
15 – 18	solubilizing agent

Table 8

Demulsifier Cost Estimates for Emulsion-Fouled Donuts

Demulsifier	Temperature	Percent Req'd	No. Barrels Per 26,000 gal.	Approx. Cost*
MQAC (Agent L)	40°F	1.0%	5	$1,630
	75°F	0.5%	2-1/2	$ 815
	115°F	0.1%	1/2	$ 163
DCDMAC (Agents B & D)	40°F	0.8%	4	$1,184
	75°F	0.2%	1	$ 296
	115°F	0.05%	1/4	$ 74

* As of March 1976

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Table 9

Toxicity of Agents

Compound	Use	Oral LD$_{50}$ per Kg	Comments
Agent L	Demulsifier	-	No data available but may have higher LD$_{50}$ than Agents B & D because of higher M.W.
Dicocodimethylammonium-chloride (Agents B & D)	Demulsifier	1.1	Very low toxicity
Polyoxyethylene sorbitan monostearate (Tween 60)	Emulsifier	33.8	Food additive (USA)
Sorbitan monostearate (Span 60)	Emulsifier	31	Food additive (USA)
Polyoxyethylene sorbitan monolaurate (Tween 20)	Emulsifier	18	Food additive (England)

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APPENDIX

Title: Removing and Recycling Chemical Demulsifiers in the Oily Waste
Treatment Process to Reduce Costs

Objective:

To develop and evaluate a specific physico-chemical means for the
recovery of the demulsification agents used in the treatment of oily
waste thereby reducing both system treatment costs and toxicity of the
aqueous effluent before discharge into ecological waters.

Approach:

Recent work at this Laboratory has shown that cationic surface
active agents of the quaternary ammonium compound type are powerful
demulsifiers. They are (a) unaffected by pH of oily waste, (b) insensi-
tive to the nature of the oily waste, (c) incapable of re-emulsifying
oil if excess amounts are used and (d) highly effective in presence
of particulate matter. Two other properties would also be desirable;
(e) low cost per treatment and (f) low toxicity. With respect to these
last two properties the quaternary ammonium compounds fall slightly
short. However, this problem is not without a solution and the
following approach suggests itself:

(1) Examine partition of cationic demulsifiers between the concen-
trated oily waste phase and the separated aqueous phase in broken
emulsion systems.

(2) Evaluate adsorption isotherms for the cationic demulsifiers
in both the aqueous and nonaqueous systems noting those systems which
are most effective in concentrating the cationic demulsifier.

(3) Propose system, on the basis of the accumulated laboratory
data, which may be suitable for concentrating the used demulsifier for
the purposes of regenerating and recycling the agent back into the oily
waste treatment process.

Progress:

A literature survey indicates that adsorbents exist which are
specific for cationic surface-active agents. In some cases the adsorbent
may adsorb preferentially ten times as much cationic agent as anionic
material (anionics and nonionics constitute the bulk of the class of
natural and synthetic emulsifiers). Thus, a principle exists whereby

the highly effective class of cationic demulsifiers may be removed
and possibly be recycled back into oily waste treatment systems.

Plans and Milestones:

   A.   Establish distribution coefficient of cationic demulsifiers
between water and various Navy oils. Determine effect of salinity and
oil type if possible.

   B.   Determine interaction of cationic demulsifiers with a variety
of common adsorbent materials (especially those known to possess
negatively charged adsorption sites) from the aqueous phase as a function
of salinity.

   C.   Determine adsorption isotherms for cationic demulsifiers alone
and in the presence of known anionic and ionic demulsifiers.

   D.   If feasible or applicable, determine adsorption of cationic
demulsifiers from the separated oily phase.

   E.   Make preliminary recommendations for adsorbents suitable for
recycling cationic demulsifiers and write report.

Funding Level: 1 MY - $60.0 K

Personnel: 1 Ph.D.

Research Proposal II

Title: Demulsification: Mechanism of and Improved Agents for

Objective:

To determine the nature of the demulsification process in order to make more efficient use of those agents presently available and to develop even more efficient agents to further reduce oily waste treatment costs, effectively eliminating secondary processing of residue oil droplets.

Approach/Plans/Milestones

The extraordinary stability of oil-in-water and water-in-oil emulsions sometimes found in Navy bilges and ballast tanks can be traced to the development of tough interfacial layers between the oil and water contained in these emulsions. A physico-chemical investigation of such structured interfaces together with a knowledge of their sensitivity to prospective demulsification agents such as surfactants and polymers, will allow a solid foundation to be developed for the treatment of complex oily wastes. Details of the approach to be used are as follows:

(1) Develop model system which simulates emulsion behavior similar to that expected in the field.

(2) Characterize emulsion parameters such as oil characteristics (solubility parameter), emulsifier (HLB) and interfacial toughness (yield stress and elastic modulus).

(3) Observe effect of demulsifier on emulsion stability and concurrently upon interfacial characteristics making use of surface film balance and supplementary phase diagram studies.

(4) Catalog data and note interplay of demulsifier and emulsifier characteristics.

(5) Develop rules and guidelines for more efficient use of presently available demulsifying agents.

(6) Synthesize and test new classes of more efficient demulsifiers based on new rules and guidelines.

(7) Test concepts and new agents in field trials and tests.

(8) Implement new agents and systems into fleet.
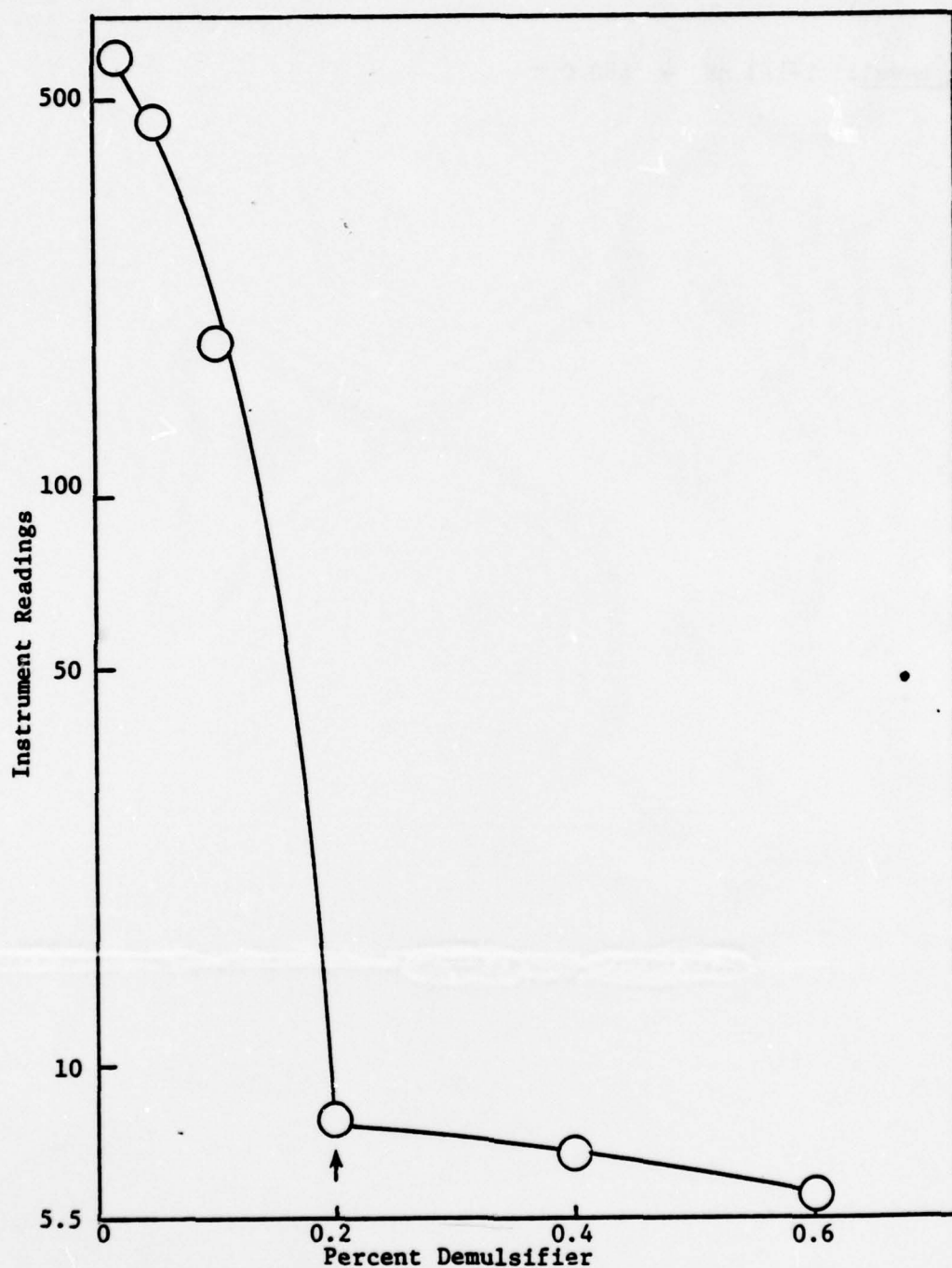
Funding Level: 1-1/3 MY - $80.0 K

Figure 1: Effect of Demulsifier (Agent L) on a 5% oil-in-sea
water. Emulsions Stabilized with 1% Bilge Cleaner Showing
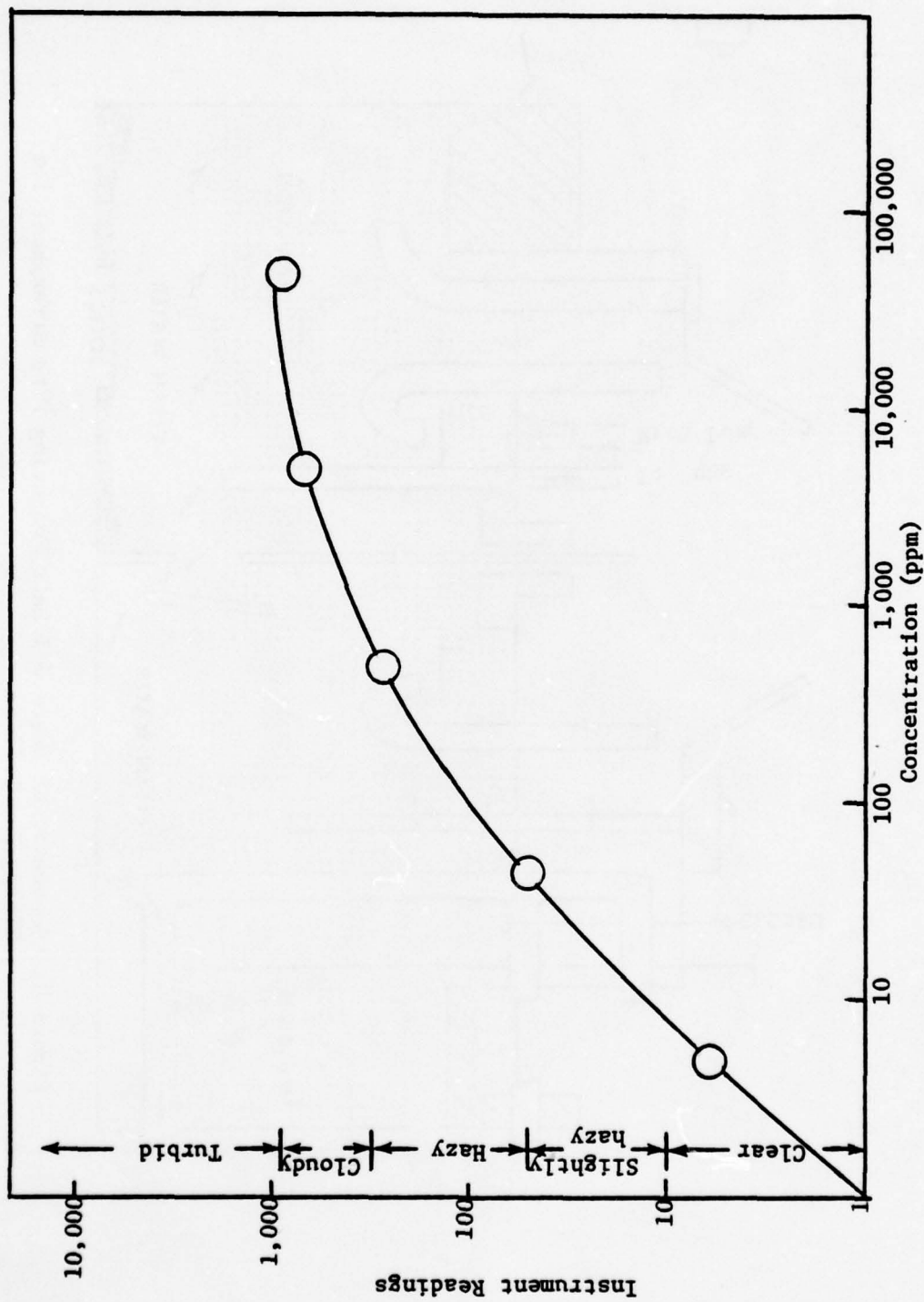Critical Demulsifier Concentration (CDC).

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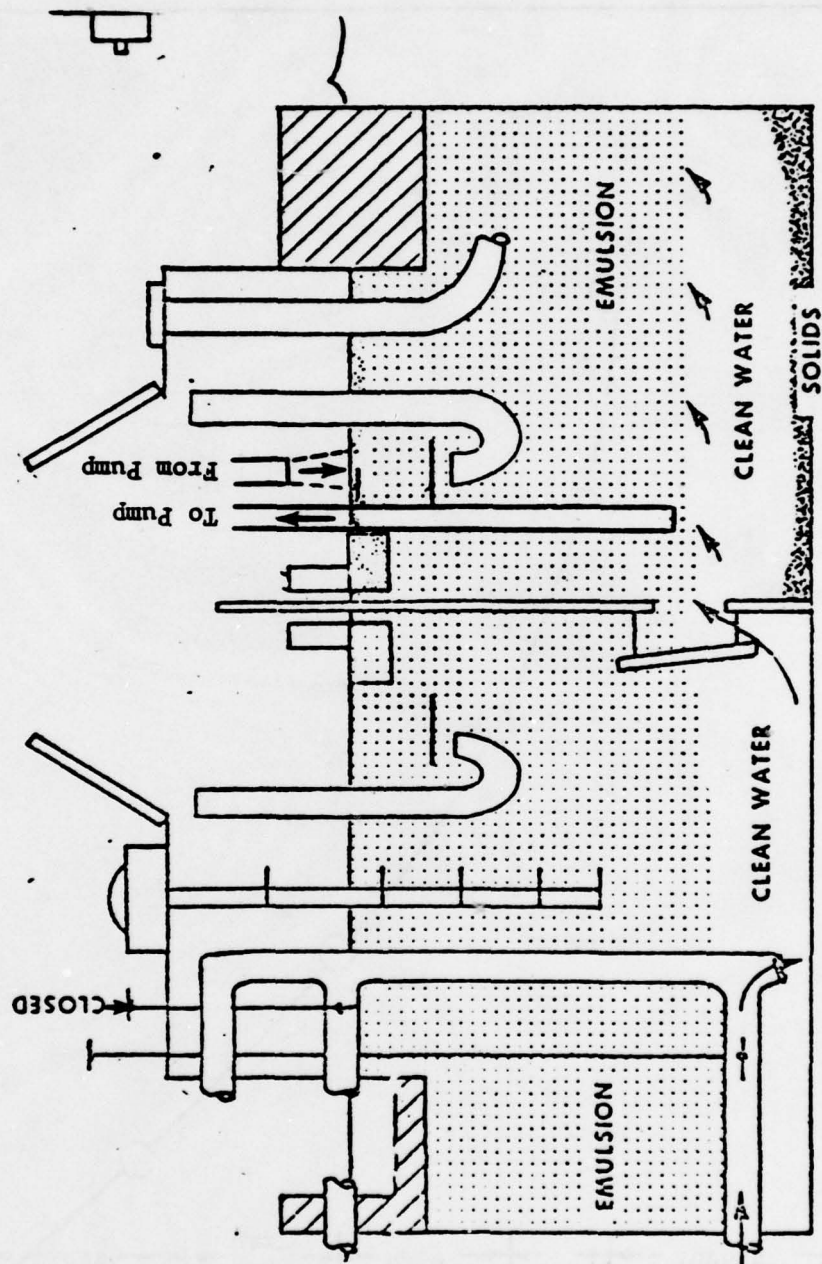Figure 2: Plot of Klett-Summerson Instrument Readings vs Oil Concentration

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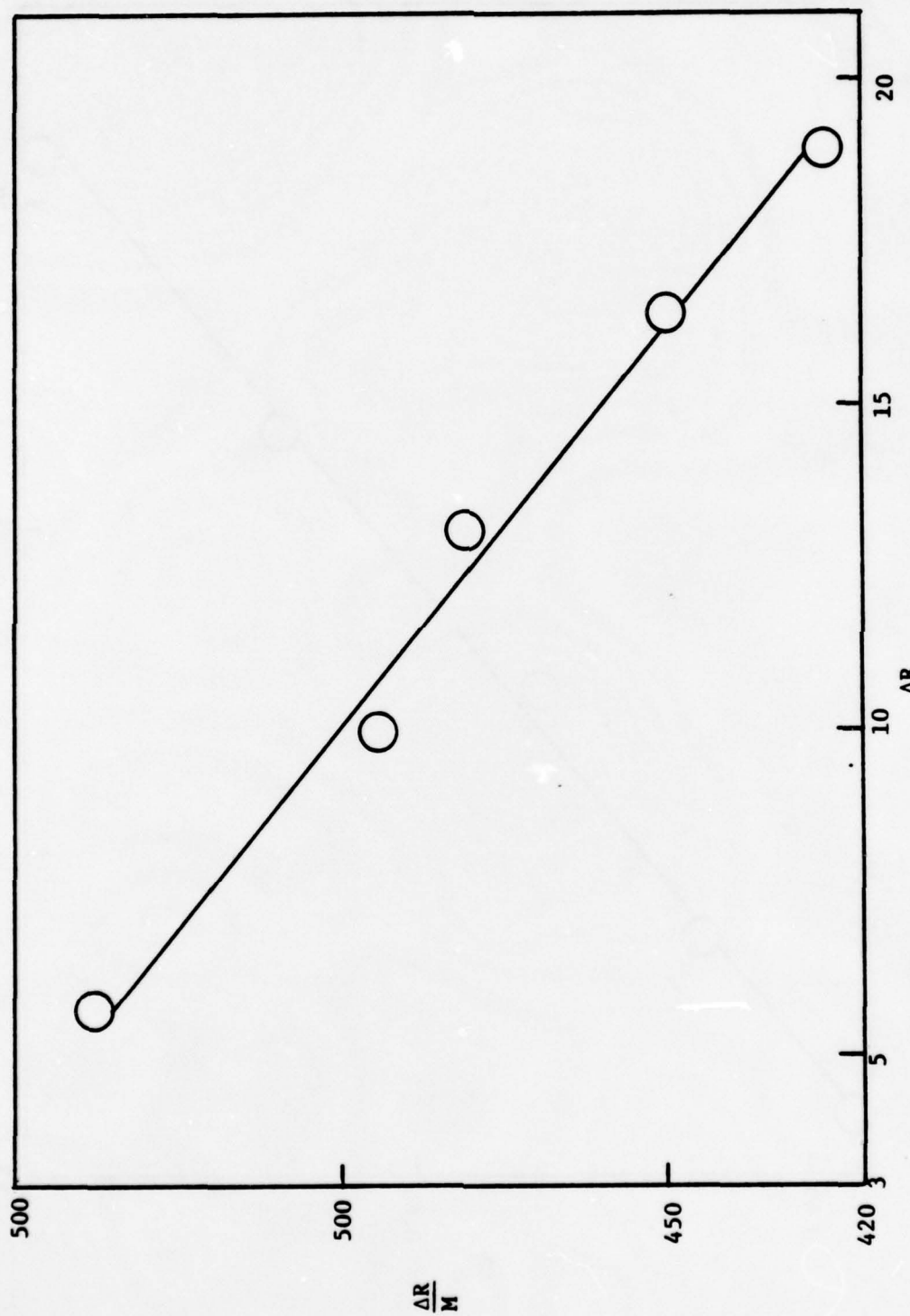Figure 3: Schematic of Waste Oil Raft Featuring Pipe Arrangment for Mixing Demulsifier

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Figure 4: Vapor Pressure Osmometry of Dicocodimethylammonium Chloride in Acetone
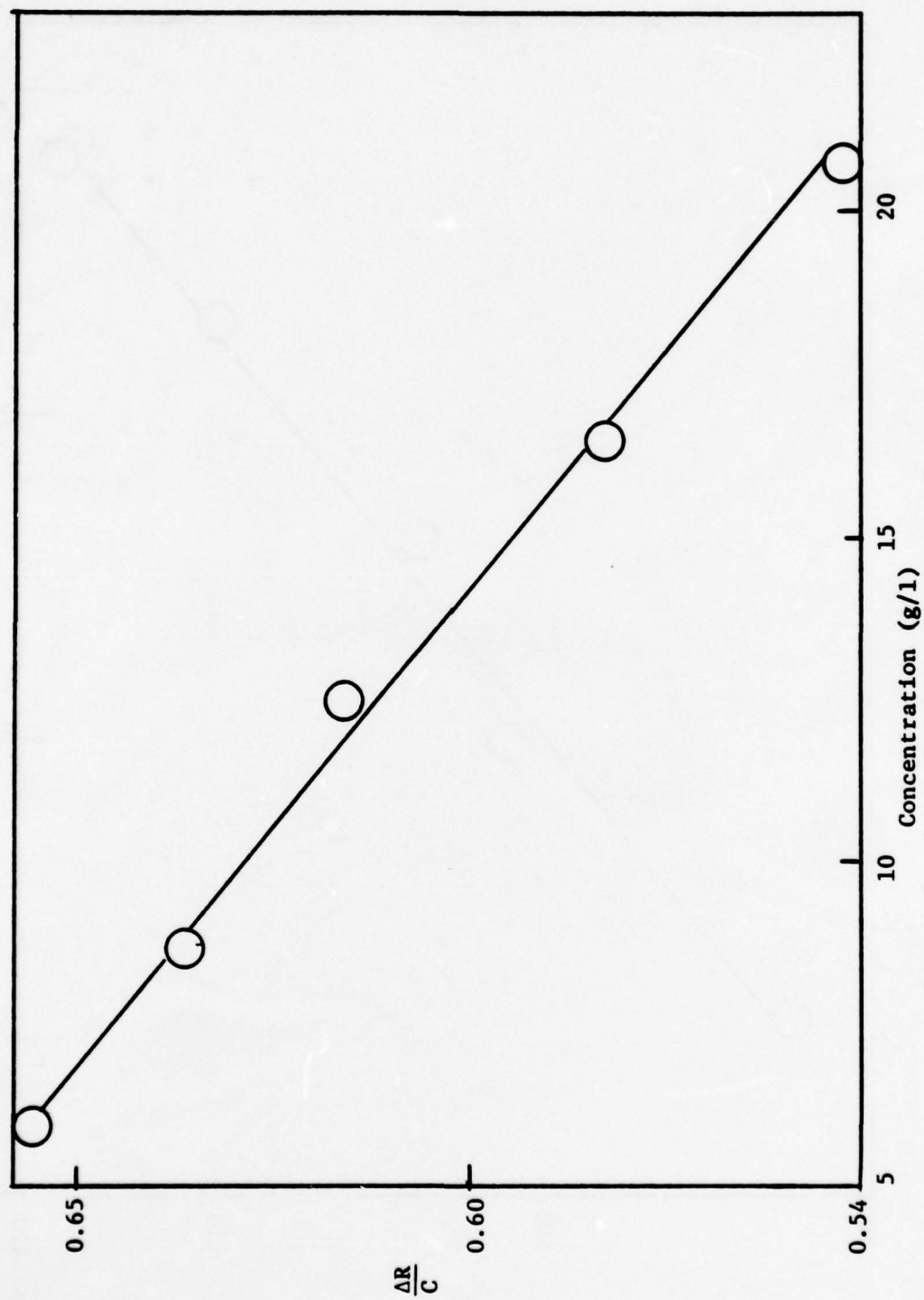
Figure 5: Vapor Pressure Osmometry of Agent L in Acetone

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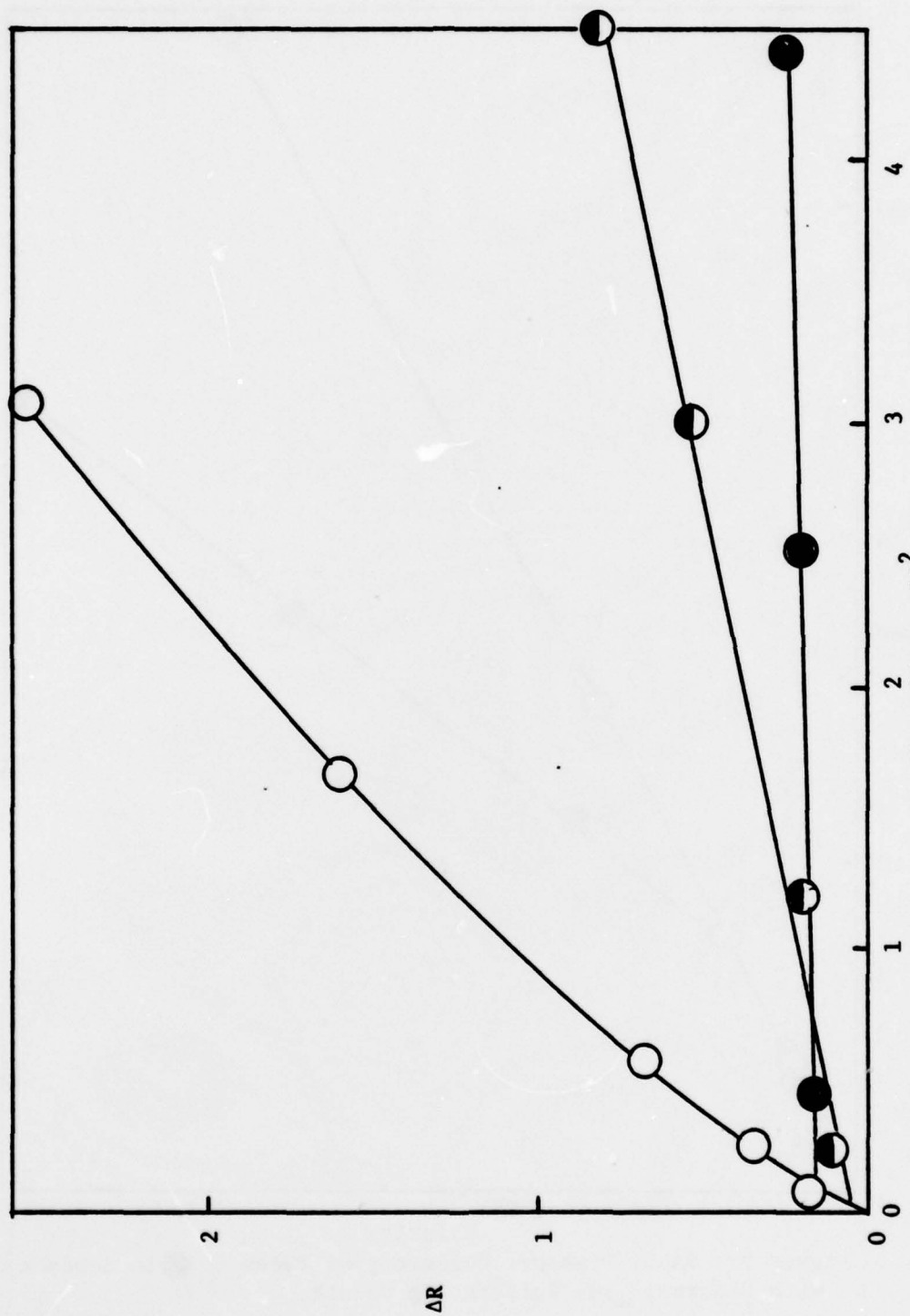
Figure 6: Vapor Pressure Osmometry of Tween 85 ● and Dicocodimethylammonium Chloride ◐ in Water using Sodium Chloride ◯ as Calibrating Solute.
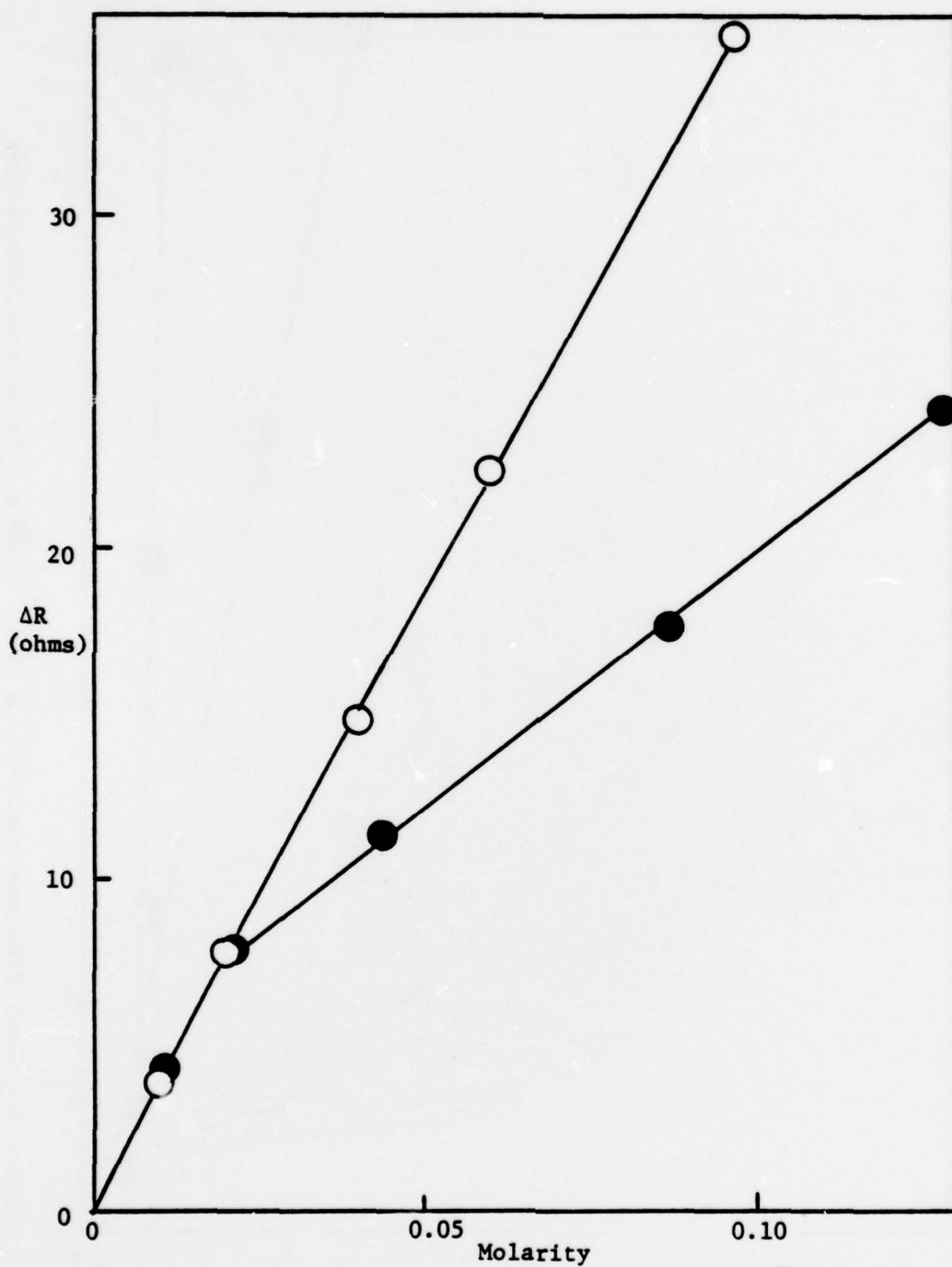
Figure 7: Vapor Pressure Osmometry of Tween 85 ● in Heptane with Biphenyl ○ as Calibrating Solute.

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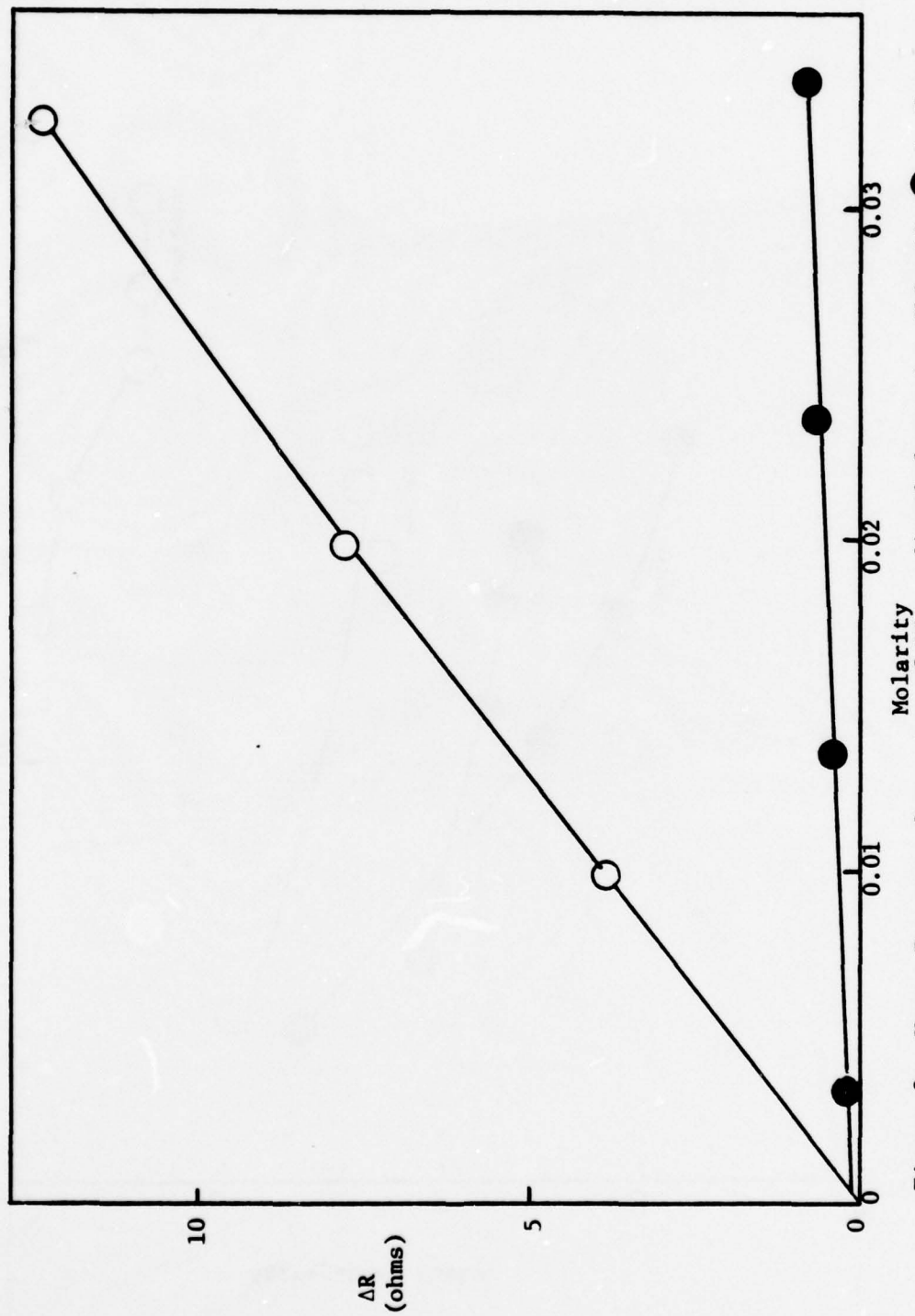
Figure 8: Vapor Pressure Osmometry of Dicocodimethylammonium Chloride ● in Heptane using Biphenyl ○ as Calibrating Solute.

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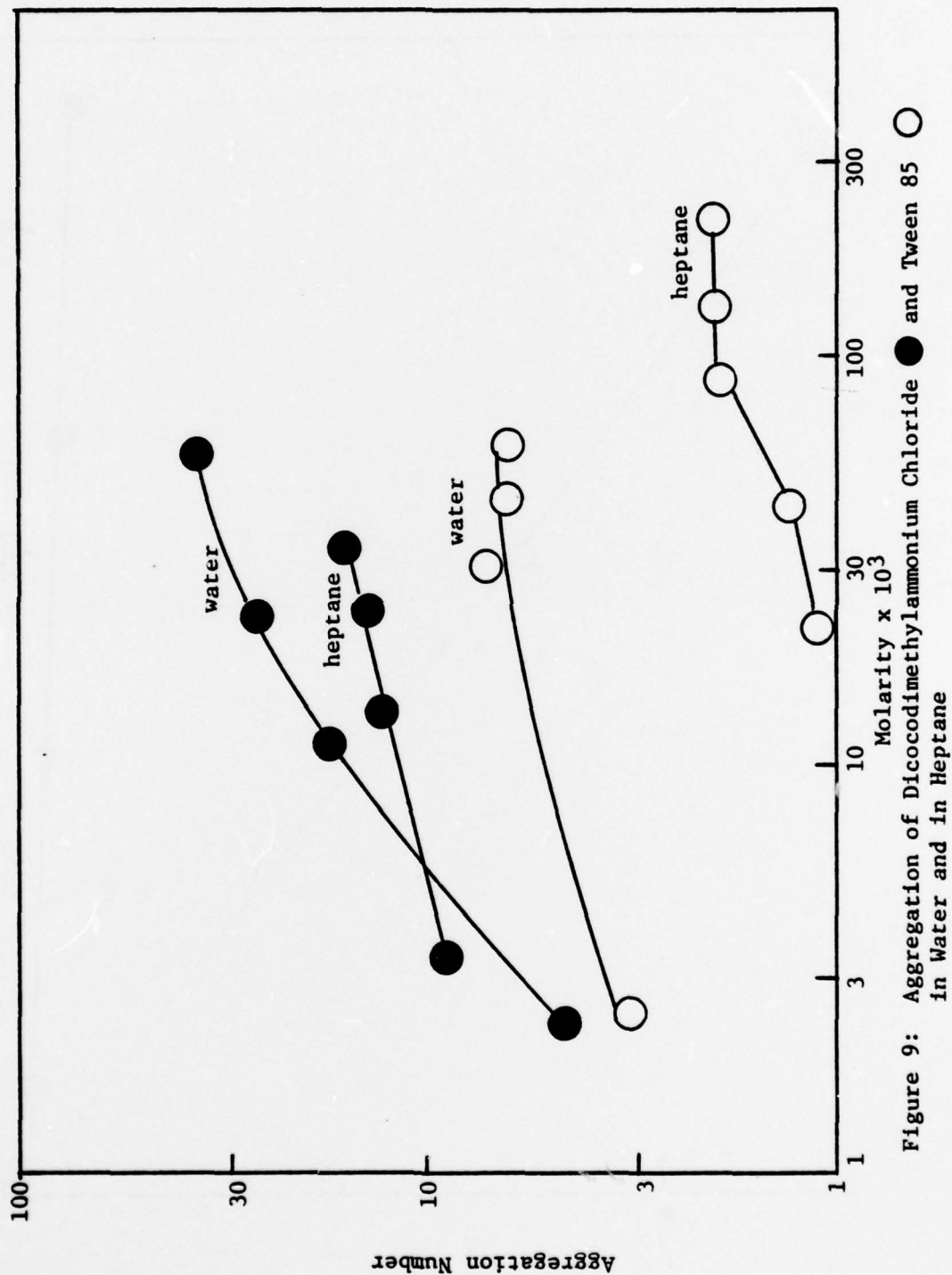
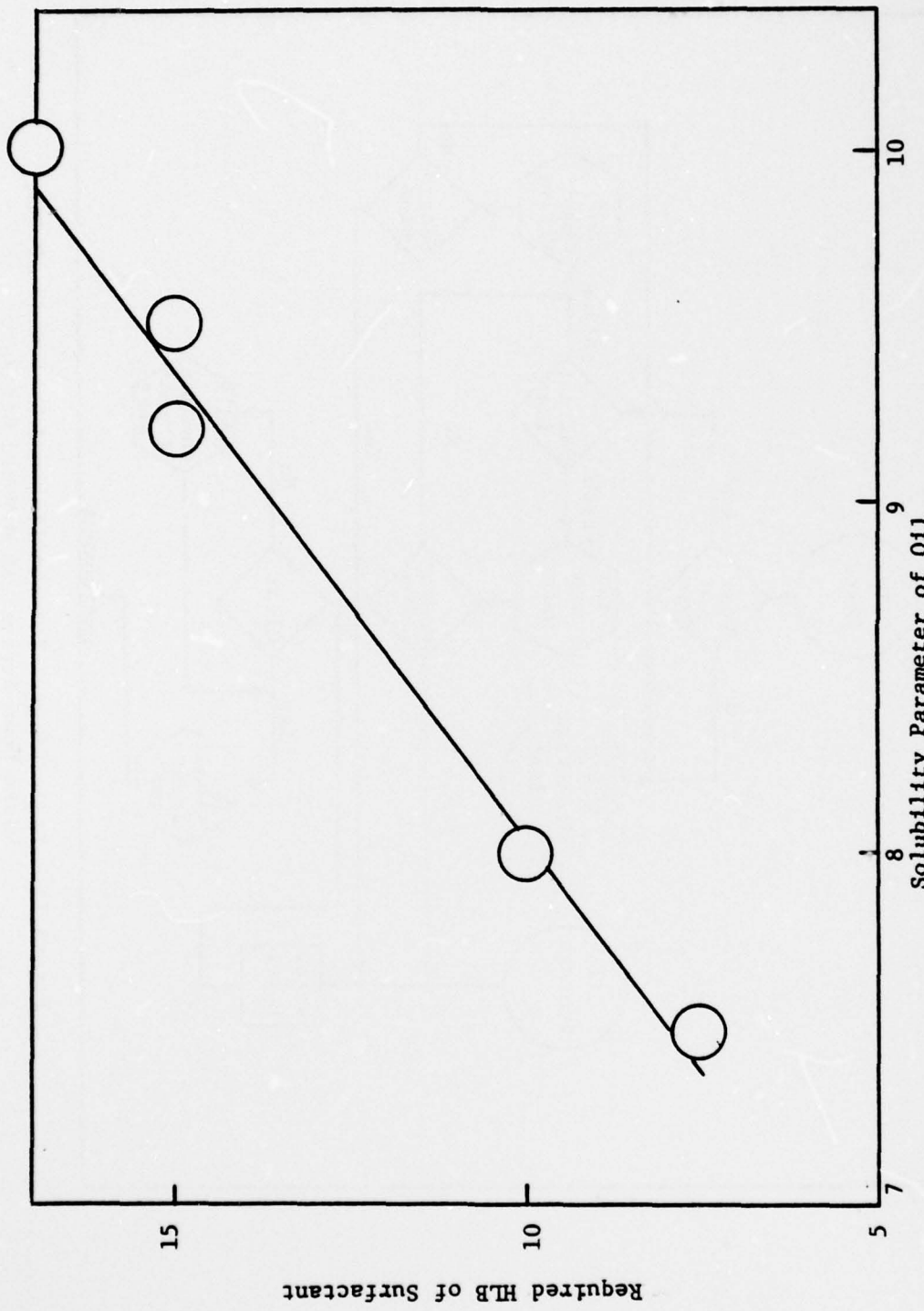Figure 9: Aggregation of Dicocodimethylammonium Chloride ● and Tween 85 ○ in Water and in Heptane

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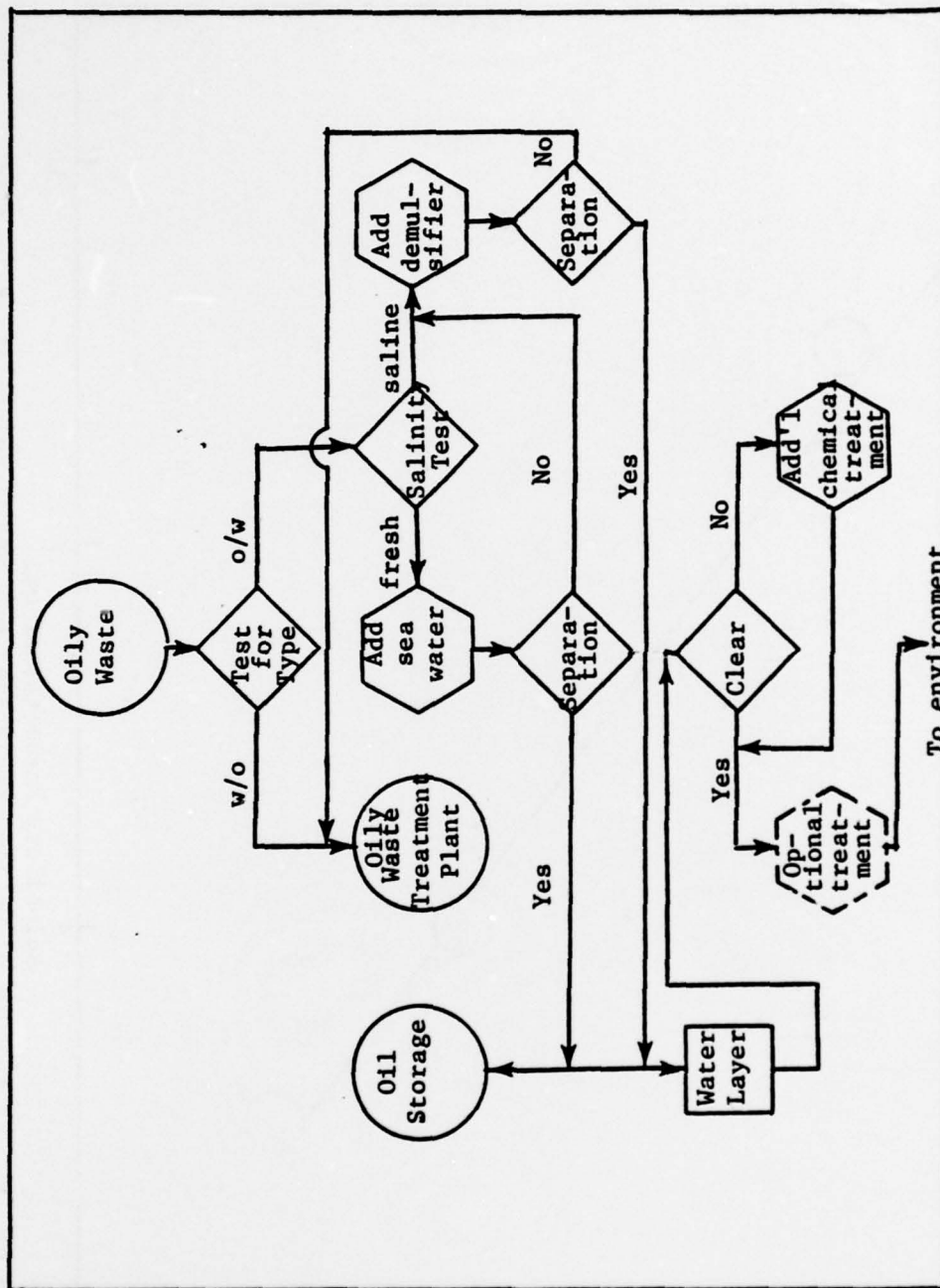Figure 10: Dependence of Optimum Emulsifier HLB on Oil Solubility Parameter

Figure 11: Logic Diagram for Handling and Treatment of Oily Waste Upon Arrival in a Waste Oil Raft
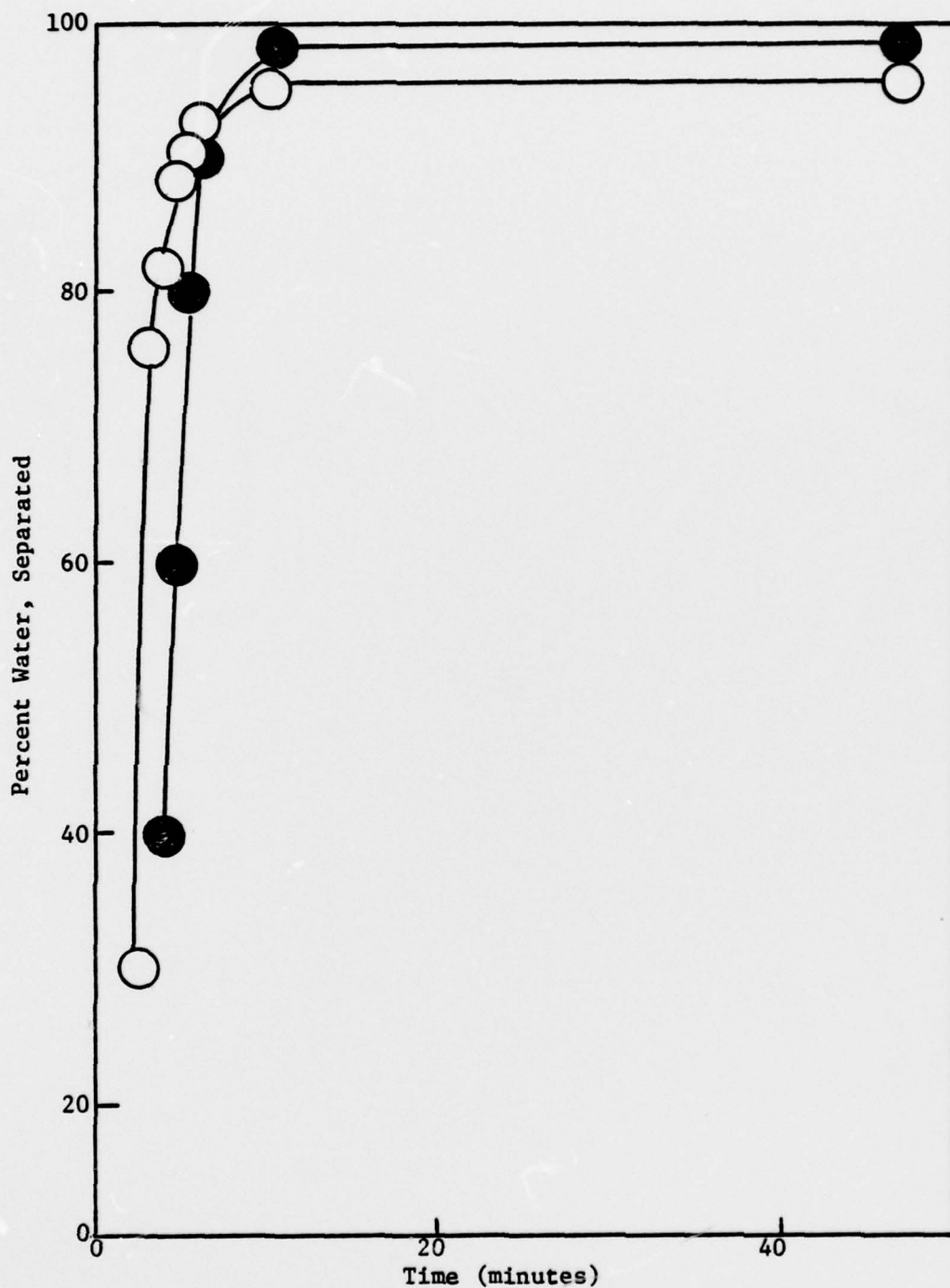
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Figure 12: Breaking Water-in-Oil Emulsions with NRL Two Part Demulsifier System at 50°F in 40 Gal. Metal can ● and 500 ml. Glass Cylinder ○.

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